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International application number: PCT/US05/002971

International filing date: 03 February 2005 (03.02.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/541,371
Filing date: 03 February 2004 (03.02.2004)

Date of receipt at the International Bureau: 03 March 2005 (03.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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APPLICATION NUMBER: 60/541,371

FILING DATE: *February 03, 2004*

RELATED PCT APPLICATION NUMBER: *PCT/US05/02971*



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Customer No. 31013

Docket No. 161485-00620

PROVISIONAL APPLICATION FOR PATENT COVER SHEET



Mail Stop Provisional Patent Application
Commissioner for Patents
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Alexandria, VA 22313-1450

This is a request for filing a Provisional Application for Patent under 37 C.F.R. § 1.53(c).

Inventor(s) and Residence (city and either state or foreign country):

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For **FOAM COMPOSITE FOR HYDROCARBON ABSORPTION AND PROCESS FOR MAKING**

1. ☒ 12 sheets of specification
2. ☒ A check in the amount of \$80.00 is enclosed in payment of the required fee. The Commissioner is hereby authorized to charge and additional fees or credit any overpayment to Deposit Account No. 50-0540.
3. ☒ Please direct all communications relating to this application to the address of:

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4. ☒ Applicant hereby states pursuant to 37 C.F.R. § 1.27(c)(1) that Applicant is a small entity.
5. ☒ This invention was not made by an agency of the United States Government or under a contract with an agency of the United States Government.

Dated: February 3, 2004

Respectfully submitted,

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Docket No.: 161485-00620

PROVISIONAL APPLICATION FOR LETTERS PATENT

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Title: **FOAM COMPOSITE FOR HYDROCARBON ABSORPTION AND
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Background of the Invention

Straw or cotton or other various mixed cellulosic materials are typically used on industrial oil spills as absorbent medium. Cellulosics have a dusty character that is objectionable. These conventional oil-adsorbing materials are not ideal because the resultant weight-to-weight ratio of adsorbent material to oil absorbed is less than one-to-ten in most instances.

Granulated polystyrene foam has been used as an absorber of oil and like hydrocarbons. The oil affinity of its surface is achieved by virtue of its hydrocarbon content. However, polystyrene materials must be "blown" or produced under carefully controlled factory conditions. Methylchloride is used as blowing agent. High temperature heat sources are required for carrying out the reactions involved. Such materials are too costly for most applications.

Faudree, US Patent No. 4,230,566, teaches the production of an alcohol-grafted polyurethane for the express purpose of absorbing water-borne oil spills. After production the polyurethane is ground to a power which is applied to the spill. It is clear that while the chemistry is appropriate, grinding the polyurethane into a powder and applying it to a water-borne spill causes certain recovery problems. Grinding is necessary to increase surface area.

In patent application No. 09/387,466, Thomson teaches that an increase in surface area can be achieved by casting the polymer on the inside structure of a substantially open cell polyurethane foam. In his work, a hydrophilic polyurethane was cast on a reticulated polyurethane. The result was a high surface area, flow-through composite which does not require grinding.

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Over the recent past, as the transportation of petroleum products by sea has greatly expanded, significant oil spills have been encountered. When these spills migrate toward land, it has been necessary for governmental agencies and affected industries to carry out clean-up procedures. All such currently envisioned procedures are of questionable effectiveness. Usually, elongate floating containers fashioned of inexpensive oil adsorbents within a perforate retainer or casing are formed as adsorbant booms in a line and floated against the oil slick to gradually confine and collect it. Typical adsorbent materials used within these devices are essentially the same as described above in connection with industrial oil spills. These, in addition to having the noted relatively low oil pick-up ratio, tend to adsorb water and sink after a limited period of use. The costs encountered in transporting the very light adsorbing materials to the site of an oil collecting activity are prohibitive in view of the low density/high volume of the materials involved.

Summary of the Invention

The present invention is addressed to a new, low density, polymeric medium for adsorbing hydrocarbons insoluble in water with significantly enhanced efficiency. The material readily absorbs contaminant hydrocarbons on weight-to-weight bases of about 20:1. The new material is producible utilizing the method and system of the invention, under a broad range of ambient temperatures and at costs competitive with the least expensive materials of lower efficiency heretofore available in the market.

A low-density cellular polyurethane polymer is provided having excellent water-insoluble hydrocarbon absorption characteristics. It is produced by first reacting a polyisocyanate with a long-chain monohydric alcohol or mixture of long-chain monohydric alcohols of about 8 to 12 carbon atoms to form a prepolymer. The prepolymer is then reacted with a polyol. Before

any substantial reaction of this mixture takes place, it is applied to a substantially open-cell polyurethane foam so as to coat the inside structure.

The material provided has a high capacity for adsorbing water-insoluble hydrocarbons such as oil and grease. Further, the material is characterized by a low absorption of water, thus improving its utilization as a material for treating water-borne oil spills.

The advantage of the medium resides in the high surface area and flow-through characteristics of the open-celled foam that serves as the scaffold on which the oil absorbing prepolymer/polyol reaction mixture is deposited.

Brief Description of The Drawings

Fig. 1 is a representation of the instant invention as an oil absorbing coating on a substantially open-cell foam.

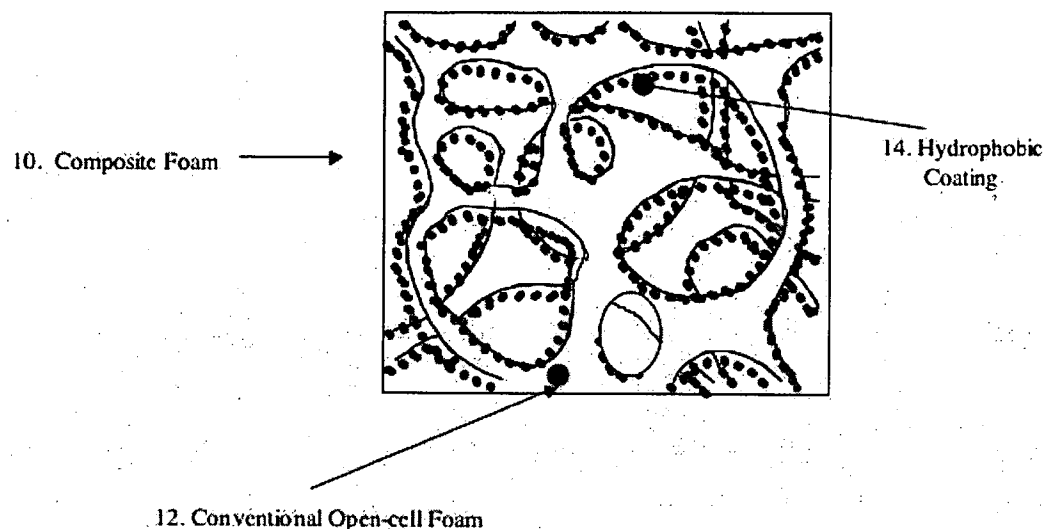
Fig. 2 is a block flow diagram of the process of the invention;

Detailed Description of the Invention

Polyurethane foams having a broad range of physical characteristics have been produced by industry. The procedures generally utilized for preparing isocyanate terminated prepolymers and reacting these polymers to produce a rigid cellular foam have been described extensively. See for example, Saunders and Frisch, "Polyurethanes: Chemistry and Technology, II Technology" pp. 193-239, Interscience Publishers, New York 1964.

Referring to Fig 1, the instant invention is a composite 10 composed of an open-celled polyurethane scaffold 12 on which a polyurethane coating containing long-chain 14 alcohols have been 14 applied.

Figure 1: Conventional Reticulated Foam with Hydrophobic Coating



With reference to Fig 2, the procedures for carrying out the process of the invention are outlined. Block 20 identifies a prereaction step wherein polyisocyanate is reacted with a linear, monohydric alcohol to create the hydrocarbon affinity of the product. Block 22 shows the addition of $C_3 - C_{12}$ alcohol. Block 24 is the reaction step. The alcohol is a long chain monohydric alcohol or mixture of alcohols of about 8 to 12 carbon atoms per molecule and the prereaction results in the formation of a prepolymer.

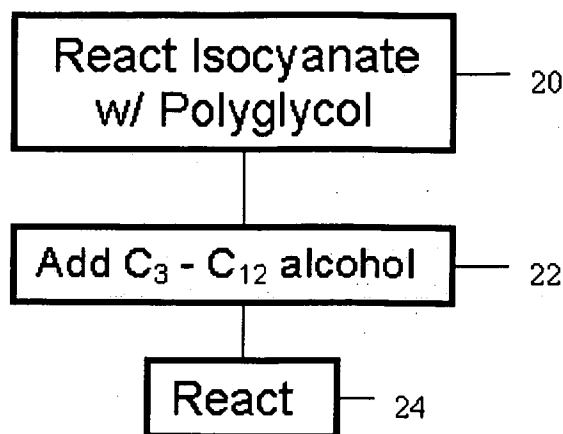


Figure 2

Greater surface affinity for oils or similar contaminant hydrocarbons can be achieved by increasing the average number of such carbon atoms, per molecule. However, as that number is increased, longer reaction times are encountered which tend to lessen the practicality of the process as is achieved with the C₈ -C₁₂ alcohols.

The amount of alcohol employed is about 10% to 25% of the stoichiometric amount that would be required for complete reaction with the polyisocyanate. The amount of alcohol employed with respect to the weight of the polyisocyanate is important for achieving high absorbancies. Where the alcohol content, for instance, utilizing C₁₀ - C₁₂ alcohol mixes is maintained between about 5 and 15% by weight of polyisocyanate, high absorbancies are achieved. Particularly, highest absorbancies are obtained where C₁₀ -C₁₂ mixed alcohols are provided at about 11% by weight polyisocyanate. The following tabulation shows absorbancy data for a range of such alcohol contents:

| % Available | Absorbancy |
|--------------------|---------------------|
| | * |
| NCO Reacted | Ratio(weight basis) |
| 0.10% | 28.7:1 |
| 5.30% | 29.8:1 |
| 11.10% | 34.4:1 |
| 12.90% | 25.5:1 |

*Absorbancy Ratio is defined as the weight in pounds of SAE 30 motor oil absorbed by 1 pound of the test material.

In Figure 2, the prepolymer compounded in block 10 is mixed in block 12 and reacted with the C₃ – C₁₂ alcohol in block 24. Once the polyol is mixed with the prepolymer, a limited time frame or period is available to the operator to dispense the mixture onto the open-cell foam. Application of the mixture onto the web of open cell foam should be carried out before any significant reaction commences. The reaction mixture is immediately forced into the open-celled foam by means of pinch rollers or scrapers or similar devices to ensure that the mixture is evenly distributed through-out the open-celled structure. A curing period follows followed by packaging.

The linear monohydric alcohol serves to increase surface affinity for hydrocarbons and, in view of its linear nature, serves to promote flexibility to the polyurethane product due to a built-in plasticizing property of long chain alcohols.

Polyisocyanate employed in the preparation of the prepolymer is readily commercially available and comprises an aliphatic, cycloaliphatic, or aromatic polyisocyanate having preferably from two to five isocyanate groups. If desired, mixtures of polyisocyanates can be employed. Suitable polyisocyanates include the aliphatic polyisocyanates such as hexamethylene diisocyanate, alicyclic polyisocyanates such as 4,4' dicyclohexylmethane diisocyanate, and

aromatic polyisocyanates such as 2,4- and 2,6-tolylene diisocyanate, diphenylmethane diisocyanate, and the dimethyl derivatives thereof. Further examples of suitable polyisocyanates are 1,5-naphthalene diisocyanate, triphenylmethane triisocyanate, xylylene diisocyanate, and the methyl derivatives thereof, polymethylene polyphenyl isocyanates, chlorophenylene-2,4-diisocyanate, and the like. The preferred polyisocyanates are aromatic polyisocyanates and particularly diphenylmethane diisocyanate, triphenylmethane triisocyanate, polymethylene polyphenylisocyanate, complex commercially-available compositions containing polymeric isocyanates sold under such trademarks as "PAPI", "Mondur MR" and "NCO-120" and mixtures thereof.

Typical polyols used as described in connection with block 12 include: ethylene glycol; propylene glycol; butylene glycol; glycerol; trimethylolpropane; trimethylolethane; 1,2,6-hexanetriol; pentaerythritol; diethylene glycol, dipropylene glycol; and the like. Typical dicarboxylic acids include: adipic acid, succinic acid, azaleic acid, phthalic acid, isophthalic acid, terephthalic acid, chlorendic acid, tetrabromophthalic acid and the like, and the corresponding anhydrides where such anhydrides exist. Also, long chain dimer acids may be used to form useful polyols by esterification with polyols, especially diols such as ethylene glycol and the like. For the purposes of this invention, useful polyesters should have a minimum hydroxyl number of about 200, and preferably above about 250, with best results being obtained from those polyesters having hydroxyl numbers in excess of about 300.

Another useful class of polyols which can be employed are the trialkanolamines which, by reaction with alkylene oxides, form adducts of suitable molecular weight, and the alkylene oxide adducts thereof. Illustrative of the lower molecular weight trialkanolamines include triethanolamine, triisopropanolamine and tributanolamine. The alkylene oxide adducts which can

be employed are preferably those wherein the oxyalkylene moieties thereof have from 2 to 4 carbon atoms.

Another useful class of polyols which can be employed are the alkylene oxide adducts of mono- and the polyamines and also ammonia. These may be termed aminic polyols.

The mono- and polyamines are preferably reacted with alkylene oxides which have 2 to 4 carbon atoms, for example, ethylene oxide; 1,2-epoxypropane, the epoxybutanes; and mixtures thereof. Mono- and polyamines suitable for reaction with alkylene oxides include, among others, methylamine, ethylamine, isopropylamine, butylamine, benzylamine, aniline, the toluidines, naphthylamines, ethylenediamine, diethylenetriamine, triethylenetetraamine, 1,3-butanediamine, 1,3-propanediamine, 1,4-butanediamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexanediamine, phenylenediamines, toluenediamine, naphthalenediamines and the like. Among the compounds of the above groups which are of particular interest are, among others, N,N,N',N'--tetrakis(2-hydroxyethyl) ethylenediamine; N,N,N',N' tetrakis(2-hydroxypropyl)ethylenediamine; N,N,N',N'--pentakis (2-hydroxypropyl)diethylenetriamine; phenyldiisopropanolamine and higher alkylene oxide adducts of aniline, and the like. Others which deserve particular mention are the alkylene oxide adducts of aniline or substituted aniline/formaldehyde condensation products.

A few of the foam formulations described herein require no catalyst. Such formulations will contain rather substantial quantities of such amino hydrogen donors triethanolamine, or other such highly reactive nitrogen containing compound. Most foam formulations described herein will require a catalyst, preferably an amine compound such as triethylene diamine, bis (2-dimethylaminoethyl) ether and metallic soaps such as dibutyltin dilaurate or stannous octoate.

The foam that serves as the scaffold for the oil absorbing polyurethane will be of the general class known as open-cell foam. A preferred embodiment is the sub-class known as reticulated polyurethane foams.

So-called reticulated foams are useful in the present invention and are typically produced by the so-called "one-shot" process wherein all of the ingredients are mixed in a single step to produce the final foam product. Using heat and pressure in specially designed vessels, a flexible skeletal foam structure without cell membranes is produced.

The open-pore structure can be produced in a range of precisely controlled pore sizes that contain void volumes of up to 98% and surface areas of up to $2000 \text{ ft}^2/\text{ft}^3$. Various pore sizes, typically from 4 to 100 pores per linear inch (ppi) enable the use of the hydrophobic polyurethane in specific applications. The high porosity of this material also helps control permeability and adds to design flexibility.

Among the benefits of reticulated hydrophobic polyurethane foams are easy fabrication and chemical resistance. Such reticulated foams also exhibit high tensile strength, elongation and tear properties that allow such fabrication techniques as cutting, shaping, stapling, tacking, stitching, cementing, laminating and grommeting. The reticulated hydrophobic polyurethane is supplied in sheets, rolls, die-cuts, and complex compound shapes. Hydrophobic polyurethane foams which have been found suitable for use in the foam composite of the present invention include without limitation those marketed under the trademarks Crest Foam and FoamEx. These products are commercially available from Crest Foam, Moonachie, New Jersey, USA and Foamex, Eddystone, Pennsylvania, USA.

There are many commercial applications for substantially reticulated hydrophobic polyurethane foams. Generally, these applications are based on properties such as the unusual physical strength of the hydrophobic foam, controlled pore size, and surface area.

The resulting foam composite of the present invention has a density from about 0.03 g/cc to about 0.10 g/cc. Its pore size distribution varies from about 8 pores per linear inch (ppi) to about 100 ppi. In a preferred embodiment the pore size distribution is from about 10 ppi to about 45 ppi, where the ratio of the weight of the open cell hydrophilic polyurethane coating to the weight of the hydrophobic foam is from about 0.01 to about 15, and preferably from about 0.5 to about 10 depending upon the application for which the foam composite has been engineered. The surface area of the foam composite of the invention varies from about 100 ft²/ft³ to about 2000 ft²/ft³ and preferably from about 300 ft²/ft³ to about 2000 ft²/ft³.

EXAMPLE 1

An alcohol reacted prepolymer was made by reacting dodecanol with an isocyanate prepolymer supplied by Chemron Corporation, Paso Robles, CA, according to US Patent 4,230,566. It was mixed with a polyol also supplied by Chemron Corporation in a ratio of 20 parts prepolymer to 1 part polyol. Immediately after mixing it was poured onto a piece of 35 ppi reticulated foam (FoamEx S-35, Eddystone, PA). The prepolymer/polyol mixture and the foam was mechanically kneaded so as to fully coat the inside structure of the reticulated foam and thus created a uniform coating of the reticulate. The sample became tack-free in 30 minutes at ambient temperature.

EXAMPLE 2

The sample produced in Example 1 was cut into pieces and subjected to a number of experiments.

A drop of SAE 30 motor oil was placed in the surface of a water bath. It immediately soaked into the treated reticulated foam. This was compared to a piece of untreated reticulated foam. The oil failed to penetrate the untreated foam.

A pan was filled half way with seawater. SAE 30 weight oil was added until it completely covered the surface. The thickness of the oil layer was about 1 mm. A piece of treated reticulated foam prepared in Example 1 and a piece of untreated reticulated foam were placed on the surface simultaneously. Visual inspection revealed that the foam produced in Example 1 soaked into the oil layer immediately while the reticulated foam resisted absorbing the oil.

EXAMPLE 3

A weighed sample of the material prepared in Example 1 was placed in a bottle of water and 30-weight motor oil. The bottle was capped and shaken mechanically for 30 minutes. The samples were carefully removed and weighed. They were then dried at 75°C for 1 hour and reweighed. The same test was also conducted on a samples of a commercially available non-woven reported to be used as an oil absorbant pad. From these data, the amount of water and oil absorbed by the product was calculated. The following table reports the results:

| | Oil | Water | O/W |
|-----------------------|-----|-------|-----|
| Treated Polyurethane | 57 | 22 | 2.6 |
| 3M Commercial product | 31 | 34 | 0.9 |
| Untreated Reticulate | 15 | 11 | 1.4 |

While reticulate foam is used herein, a so-called non-woven could also be coated with the alcohol modified polyurethane.